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π -Conjugated Radical Cations Stabilized by Surrounding Bicyclic σ -Frameworks
(ORGANIC MATERIALS CHEMISTRY-High-Pressure Organic Chemistry)

AUTHOR(S):

Komatsu, Koichi; Nishinaga, Tohru; Matsuura, Akira; Wakamiya, Atsushi

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π -Conjugated Radical Cations Stabilized by Surrounding Bicyclic σ -Frameworks

Koichi Komatsu, Tohru Nishinaga, Akira Matsuura and Atsushi Wakamiya

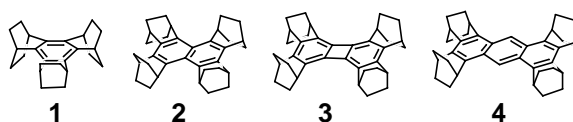
Benzene **1**, naphthalene **2**, biphenylene **3**, and anthracene **4**, fully annelated with bicyclo[2.2.2]octene were transformed into the corresponding radical cations, and their structures were clarified by X-ray crystallography. The remarkable stability of these salts are ascribed to the electronic and steric effects of the bicyclic frameworks. 1,4-Dithiin **5** annelated with the same bicyclic units was also oxidized into the stable salt of the radical cation, and the structure examined by X-ray crystallography. The ESR study indicated that the spin is effectively delocalized into the bicyclic frameworks. Dithiin **5** was further oxidized into the dication, which was shown to be 6π aromatic by the NMR and theoretical studies.

Keywords: cyclic voltammetry / X-ray crystallography / ESR / molecular orbital calculations

Organic radical cations have been of fundamental interest to organic as well as physical chemists in a variety of contexts. Their stabilization have in general been achieved by the extension of the π -conjugated system. In our group, however, it has been clarified that the remarkable stabilization of such a positively charged π -conjugated system can be attained by structural modification with σ -frameworks. Typical examples are demonstrated by the following studies.

1. Radical Cations of Benzenoid Aromatics.

A series of benzenoid aromatics, benzene **1** [1], naphthalene **2** [2], biphenylene **3** [3], and anthracene **4** [4], fully annelated with bicyclo[2.2.2]octene (abbreviated as BCO) exhibited reversible oxidation waves at remarkably



low potentials (+1.08, +0.33, +0.25, and +0.17 V in tetrachloroethane vs Fc / Fc^+ , respectively). Accordingly these hydrocarbons were readily converted to the corresponding radical cation salts, $\text{Ar}^+\text{SbCl}_6^-$, quantitatively by one-electron oxidation with 1.5 equivalents of SbCl_5 .

The salts were isolated as ruby red (**1** $^+$), dark green (**2** $^+$), blue violet (**3** $^+$), and dark green (**4** $^+$) crystals, which were stable in air at room temperature. This is the first examples of the isolation of the radical cation salts of alkyl-substituted benzene, naphthalene, and biphenylene as stable crystals. This stability is ascribed

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Scope of Research

Fundamental studies are being conducted for creation of new functional materials with novel structures and properties and for utilization of high pressure in organic synthesis. The major subjects are: synthetic and structural studies on novel cyclic π -systems having σ - π conjugation; synthesis of redox-active dehydroannulenes; chemical transformation of fullerene C_{60} ; mechanochemical reactions of fullerenes.



Prof
KOMATSU
Koichi
(D Eng)



Instr
MORI
Sadayuki
(D Eng)



Instr
NISHINAGA
Tohru
(D Eng)



Instr
MURATA
Yasujiro
(D Eng)

Students:

MATSUURA, Akira (DC)
FUJIWARA, Koichi (DC)
IZUKAWA, Yoshiteru (DC)
KATO, Noriyuki (MC)
WAKAMIYA, Atsushi (MC)
ITO, Miho (MC)
NODERA, Nobutake (MC)
INOUE, Ryouta (UG)
SUZUKI, Mitsuharu (UG)

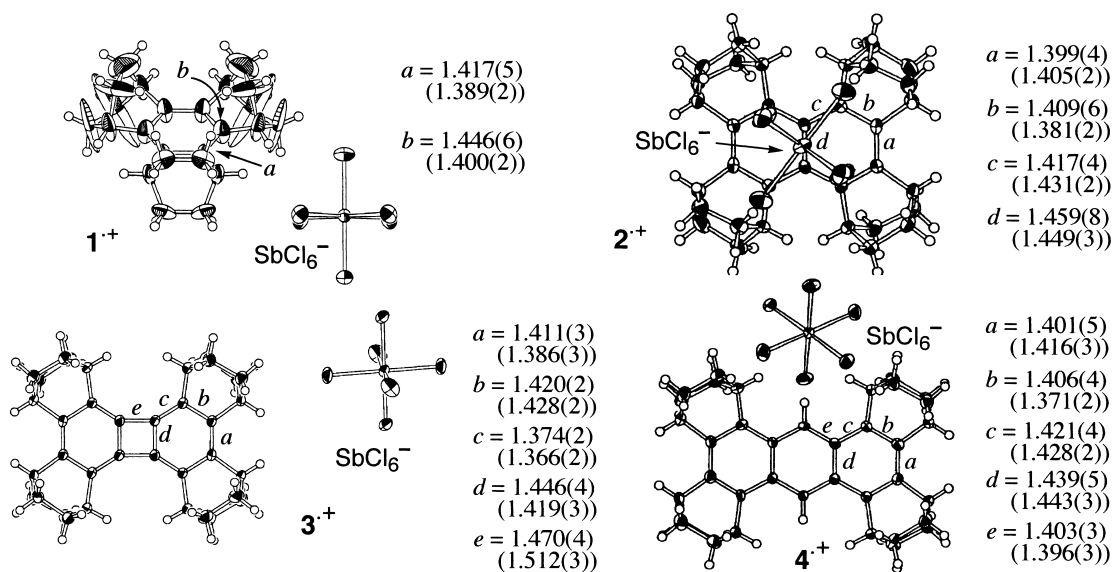


Figure The X-ray crystal structures of 1^+SbCl_6^- – 4^+SbCl_6^- with the averaged bond lengths. The values in the parentheses are the bond lengths of the neutral molecules.

to both the electronic effects, such as inductive and σ - π conjugative effects, and the steric effects, such as steric and “Bredt’s rule” protection, of the rigid bicyclic σ -frameworks surrounding the π -system.

The X-ray crystallography was conducted for these radical cation salts to give the results shown in Figure. Here the change in bond lengths upon one-electron oxidation of **2–4** is related to the coefficients of the relevant carbons’ HOMO of the neutral molecule: the bonds with the bonding nature in HOMO were elongated and those with antibonding in HOMO were shortened. The benzene radical cation appears to be subjected to the static Jahn-Teller distortion, although the effect of crystal packing force can not be completely ruled out.

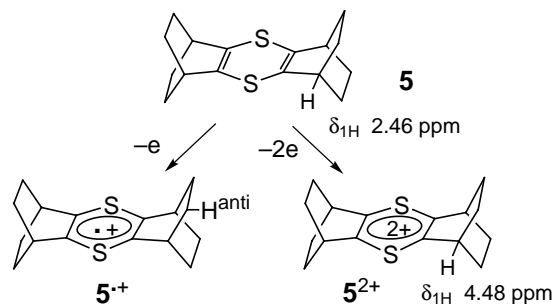
2. Radical Cation and Dication of 1,4-Dithiin [**5**, **6**].

The 1,4-dithiin is a π -conjugated system isoelectronic to cyclooctatetraene, and its derivative annelated with BCO (**5**) is highly susceptible to the consecutive one-electron oxidation as shown by the oxidation potential in dichloromethane: $E_{1/2}$ (**1**) +0.0 V, $E_{1/2}$ (**2**) 0.82 V vs Fc / Fc⁺.

The oxidation with SbCl₅ afforded the radical cation salt 5^+SbCl_6^- as brown-colored crystals, which were characterized by X-ray crystallography.

The ESR spectrum of 5^+ exhibited a 9-line signal due to the coupling with 8 anti-methylene protons (a_{H} 0.080 mT) and also a weak coupling with ³³S (natural abundance 0.75%) (a_{S} 9.86 mT). The a_{S} value was even smaller than the value reported for the thianthrene radical cation (**6**). This is supported by the spin density calculated (B3LYP / 6-31G*) for these two sulfur atoms (spin density 0.2869 for 5^+ , 0.2874 for 6^+), and indicates that the bicyclic σ -framework is even more effective for spin delocalization than the annelated benzene π -system [5].

The treatment of dithiin **5** with an excess amount of a stronger oxidant, SbF₅, in CD₂Cl₂ caused the formation of dication 5^{2+} as examined by ¹H and ¹³C NMR spectroscopy. The downfield shift ($\Delta\delta$ 2.02 ppm) of the bridgehead proton of the BCO unit clearly demonstrates the presence of 6π -electron aromaticity in dication 5^{2+} . This was further supported by the value of nucleus independent chemical shift (NICS) of -8.8 calculated for 5^{2+} (GIAO / HF / 6-31+G* // B3LYP / 6-31G*) [6].



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